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Reclamation of Alkali Soils with $CaCl_2$ Solutions

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In the Bet She'an Valley there are soils classified as red-brown solonetz-grumosols (ALPEROVITCH and MOR, 1968) which until now have been considered unsuitable for cultivation due to the failures of every attempt to grow crops of any nature. The main reason is apparently the lack of adequate soil aeration, resulting from poor structure, which itself is due to high sodium content in the adsorbed phase, and perhaps also to a high percentage of exchangeable magnesium.

The soils are fine-textured, with 60% clay and 20–30% silt. The main clay mineral is montmorillonite, representing 45–50% of the total clay fraction. Large amounts of chlorite and palygorskite are also present (about 20%), and the remaining clay minerals consist of calcite, kaolinite, and illite (Dr. A. ZINGER, Hebrew Univ., Rehovot, personal communication).

Exchangeable sodium percentage is only 6–8% in the upper soil layer, but increases considerably with depth and reaches 30% at a depth of 90 cm or more. Magnesium content is very high–40% of the total adsorbed cations in the upper soil layer and exceeding 50% in the lower part of the profile. Calcium percentage of total adsorbed cations is 55% in the upper soil layer, and, in contrast to sodium and magnesium, decreases with depth to a value of only 17%. Total content of soluble salts in the surface soil layer is relatively low; the electrical conductivity of the 0–60 cm layer is 0.5–1.0 mmhos/cm. On the other hand, salinity gradually increases with depth, and in the 90–120 cm layer, conductivity is 6 mmhos/cm. Low soil infiltration capacity is a direct result of the above mentioned properties.

Clay is dispersed by adsorbed sodium, especially when the latter is present in large amounts on the adsorption complex. This dispersion destroys soil structure and reduces its penetrability to water and air (KELLEY, 1951; KOVDA, 1964), but the complementary cation also has an important effect. Calcium is known to benefit the soil by creating good structure and desirable physical characteristics related to water movement, degree of swelling, etc. On the other hand, little information is available regarding the effect of magnesium, and it is not clear whether the ion is desirable and behaves similarly to calcium (United States Salinity Laboratory Staff, 1954), or whether adsorbed magnesium causes dispersion and poor aeration (SHAWRYGIN, 1935).

In order to replace exchangeable sodium with calcium one must add sufficient calcium to the soil. The cation exchange is stoichiometric and rapid, and takes place according to the exchange equation:

$$\tfrac{1}{2}\,\bar{Ca} + Na^{+} = \bar{Na} + \tfrac{1}{2}\,Ca^{++} \qquad (1)$$

where the bars indicate cations in the adsorbed phase.

In general, it is possible to increase soil penetrability to water and air by using calcium salts (BRAUSON and FIREMAN, 1960; United States Salinity Laboratory Staff, 1954).

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However, satisfactory results were not obtained with gypsum, since this is only slightly soluble in water (a saturated solution of gypsum contains 0.01 M per liter), whereas for our purpose, an extremely large amount of adsorbed ions must be exchanged. Furthermore, hydraulic soil conductivity is extremely low and the exchange process rate very slow.

The purpose of the present study is to examine the possibility of improving the impermeable soils of the Bet She'an Valley by means of calcium chloride, and discover how a given quantity of salt can be utilized to achieve as complete and rapid an exchange of soil sodium as possible. Since $CaCl_2$ is available in Israel in very concentrated solutions (6.8 N), it is possible to apply a concentrated solution directly or to dilute it with water before applying it to the field. Calculations made by MAGDOFF and BRESLER (1972) indicated that dilute solutions will be more effective in replacing Na. However, the rate of infiltration of reclaiming solution is also diminished with dilution, more water is needed for leaching out excess salt, and mechanical dilution of the concentrated solution is expensive. Thus an empirical evaluation of methods of applying $CaCl_2$ solutions seemed necessary.

Materials and Methods

Samples of red-brown solonetz grumosol soil from the Bet She'an Valley were removed from the 60–90 cm layer, over-dried, and passed through a 2 mm sieve. Four columns were filled with the soil, using a special apparatus designed to pack them at uniform density. Soil height after filling was 53–54 cm, its weight was 1558 g, and its apparent density was 1.46–1.5 g/cm^3. Details of the soil properties prior to filling are presented in Table 1. The columns were of perspex, whose transparency facilitates accurate measurement of water movement through the soil.

Table 1. The soil and equilibrium extract composition

Ion	Na	K	Ca	Mg	
Soil extract (meq/l)	27.66	0.077	2.0	1.91	SAR = 19.8
Exchangeable ions (meq/100 gm)	8.81	3.26	14.43	13.50	ESP = 22.0
pH of the soil paste	8.4				
Electrical conductivity (mmhos/cm)	3.09				

Each of the four columns was treated with calcium chloride solution containing a different concentration of the calcium ion, but the total amount of calcium added was equal in all cases and identical to the amount of adsorbed sodium (in milli-equivalents) in the soil. The treatments were as follows:

1. 7.65 g $CaCl_2$ dissolved in 20 ml water (6.8 N)
2. 7.65 $CaCl_2$ dissolved in 100 ml water (1.36 N)
3. 7.65 g $CaCl_2$ dissolved in 100 ml water (0.68 N)
4. 7.65 g $CaCl_2$ dissolved in 100 ml water (0.34 N)

The electrical conductivities of the above solutions were 158.0, 86.8, 51.3, and 28.29 mmhos/cm respectively.

Since the solution volumes were different, the columns were wetted to different depths. Afterwards, a uniform solution of 0.01 M $CaCl_2$ was added to all the columns by use of a Mariotte bottle, which maintained a constant solution head of 28 cm above soil level. The volume of leachate collected after the solution had passed through the soil was measured as a function of time. The electrical conductivity and the concentration of calcium, magnesium, and sodium in the leachate were also determined.

The above treatments were continued for a period of two months and then each of the columns was divided into nine or ten segments. The soil was dried, and the following determinations carried out: total soluble salts, pH, electrical conductivity, and composition of the adsorbed cations, by use of an EEL flame photometer for sodium and potassium and a Unicam SP 90 atomic absorption spectrophotometer for calcium and magnesium.

Results and Discussion

Rate of Flow Through the Columns

Effluent volume as a function of time is presented in Fig. 1. Flow rate of solution through the various columns as a function of the volume of cumulative solution passing through the column is presented in Fig. 2. It is evident that the flow rate depends on the

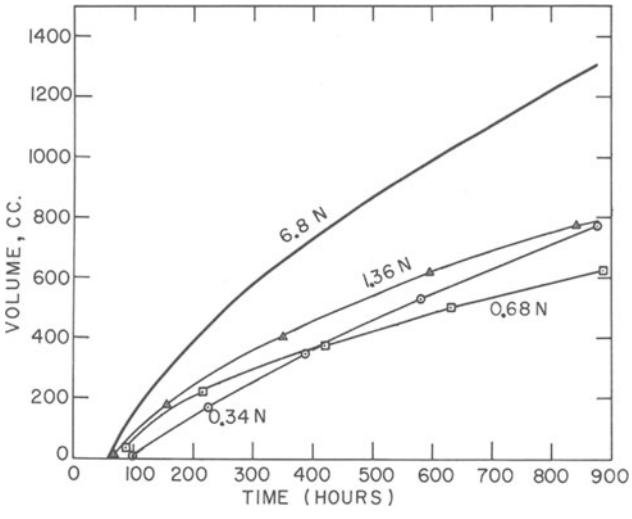

Fig. 1. Volume of effluent as function of time

concentration of $CaCl_2$ in the applied solution. The higher the concentration of $CaCl_2$ in the solution, the higher the flow rate. This might be predicted from the results of QUIRK and SCHOFIELD (1955) who found that hydraulic conductivity of soil membranes intensifies with increased salt solution concentration. They, however, applied the same solutions throughout all the inflow experiments, whereas in ours, the concentrated solutions were replaced (after the same quantity of salt had passed) by 0.01 M $CaCl_2$ solutions. Our

experiments show that high concentrations of salt, applied at the beginning of the experiments, built up stable pore structure with high hydraulic conductivity. This stability was partially lost as a result of leaching with the dilute solutions, but even after leaching with more than two pore volumes of the columns, the hydraulic conductivity of the highest concentration treatments still remained the highest, although the actual salt concentration in the effluent concentration treatments was the lowest.

The effect of concentration is masked by the effect of apparent density of soil in the column. As pointed out earlier, in spite of every precaution, the apparent density in

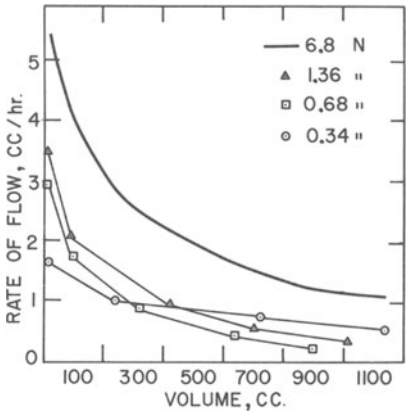

Fig. 2. The rate of flow as function of volume of effluent

treatments 1 and 4 was 1.46 gm/cc whereas in treatments 2 and 3 it was 1.5 gm/cc. At the beginning of the experiments, the effect of salt concentration was the dominant factor, and the rate of flow changed in a regular order, according to concentration. As leaching proceeded, the differential effect of concentration diminished, and the density effect became more important. Thus flow rate in the 0.34 N treatment, towards the end of the experiment, was higher than that in treatments with concentrations of 1.36 and 0.68 N.

Efficiency of Leaching Excess Salt

The electrical conductivity of the effluent, as a function of the efficient volume, is presented in Fig. 3, which shows that after flowing through the column, the concentrated solutions are somewhat diluted, due to salt diffusion and hydrodynamic dispersion, whereas the initial concentration of the dilute treatments (0.68 and 0.34 N) are increased by solution of the salt in the soil profile. Comparing the efficiency of the various treatments in leaching out excess salt from the column, it is evident from Fig. 3 that the process is most effective when the total amount of salt added is concentrated in a small volume of solution. Thus the electrical conductivity of the effluent at 0.5 and 1.0 pore volumes of the column (250 and 500 ml of solutions) shows that, at 0.5 pore volume, electrical conductivity is 8.0, 15.1, 20.5, and 24 mmhos cm^{-1} for the 6.8, 1.36, 0.68 and

0.34 N, respectively. Similarly, at 500 ml of effluent, electrical conductivity is 5.0. 6.0, 8.0 and 11.0 mmhos cm^{-1} for the above treatments respectively. Since the electrical conductivity of the leaching solution is already 2.4 mmhos cm^{-1}, the excess of water (in addition to wetting of the column) needed for leaching out the salt to 5 mmhos above the conductivity of the leaching solution, for example, is 270, 400, 520, and 650 ml for the concentration treatments of 6.8, 1.34, 0.68, and 0.34 N respectively. In terms

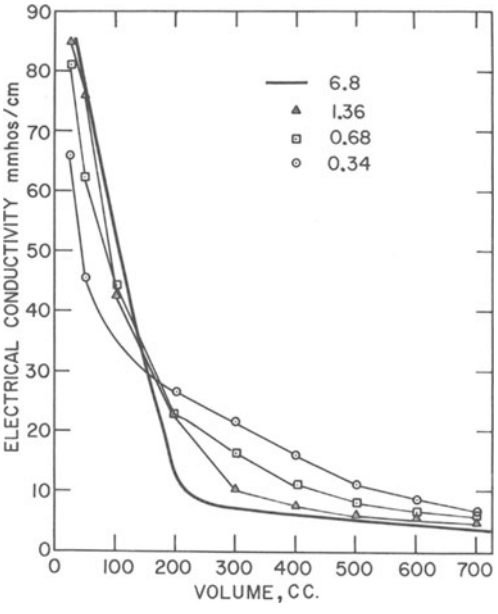

Fig. 3. The electrical conductivity of the effluent

of percent of water capacity of the column, the above values correspond to 54, 80, 104 and 130% as leaching requirements for the four treatments. The above shows that, in order to save on water for leaching out excess salt, $CaCl_2$ salt should be concentrated in as low a volume of solution as possible.

Efficiency of Na and Mg Replacement

The concentration of Na, Ca and Mg ions in the effluent was analyzed and the results are presented in Fig. 4. Table 2 shows the total amount of soluble ions in the column and in the effluent, as calculated by integration of the curves in Fig. 3. The total amounts of soluble Na, Ca, and Mg in the column are 46.5, 3.3 and 3.1 meq/column respectively and are, of course, the same for all treatments. If we recall that at field capacity the amount of water per 1558 gr of soil is about 600 cc (39%), it is evident that this soil is also saline. By leaching the soil with $CaCl_2$ solutions, the soluble ions plus the replaced exchangeable ions are found in the effluent. If we assume that the soluble ions were completely removed from the column, we can subtract their value from the total amount of ions in the

effluent and the amount of exchangeable ions replaced by the $CaCl_2$ solution is obtained (Table 2). The amounts of exchangeable Na replaced were 102.5, 92.5, 80 and 88.5 meq/column for the 6.8, 3.6, 0.68 and 0.34 N treatments respectively. The total amount of calcium introduced into each column consists of the 137 meq introduced in the concentrated solution and the amount of Ca in the leaching solution (0.01 M $CaCl_2$) that passed through the column. Since the flow rate in the 6.8 N treatment was the highest, the amount of $CaCl_2$ introduced during the two months of the experiment was also the highest (Table 2). Thus the efficiency of replacing Na (and Mg) from the column depends also on the amount of Ca introduced. This is expressed in the lowest row of figures in

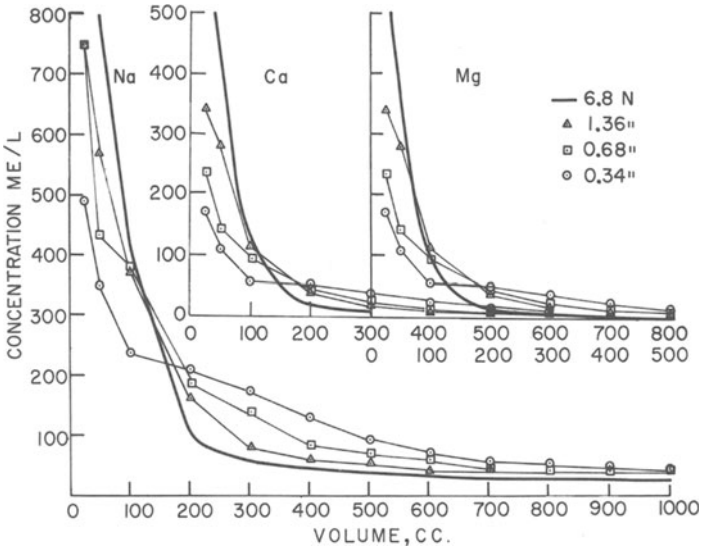

Fig. 4. The ionic composition of the effluent

Table 2, showing that the efficiency of replacing Na in the treatments was highest in the most concentrated treatment. Efficiency decreases with decrease in concentration for the 1.36 and 0.68 N treatments, but rises again with the 0.34 N concentration.

A consideration of the changes taking place in the soil profile (Fig. 5) reveal similar results. The overall changes are summarized in Table 3. The overall picture is one of reasonable agreement between the amount of exchangeable sodium found in the effluent (Table 2) and the change in sodium in the adsorbed phase (Table 3). Fig. 5 and Table 3 show that concentrated solution is again the most effective solution in replacing adsorbed Na. The percentages of adsorbed Na which was replaced are 77, 70, 63 and 66 for the 6.8, 1.36, 0.68 and 0.34 N concentration treatments respectively. This surprising result, which negates GAPON'S prediction, is discussed later.

A close scrutiny of the curves in Fig. 5 reveals that the boundary between reclaimed and non-reclaimed soil is well-defined. In the various treatments, 63 to 77% of adsorbed Na was replaced by Ca, but in all of them the amount of Na in the upper 30 cm of the

Table 2. Ionic balance in the effluent

Ion	Na				Ca				Mg			
Soluble ions in the column (me)	46.5				3.3				3.1			
	(6.8 N)	(1.36 N)	(0.68 N)	(0.34 N)	6.8 N	1.36 N	0.68 N	0.34 N	6.8 N	1.36	0.68 N	0,34 N
Soluble ions in the effluent (me)	148.5	139	126.5	135	37.0	35.0	36.8	33.3	36	31.7	38.5	33.5
Exchangeable ions in the effluent (me)	102.0	92.5	80	88.5	33.7	31.7	33.5	30.0	32.9	28.5	35.5	27.5
Soluble Ca introduced (me)[a]	163	156	150	150	163	156	150	150	163	156	150	150
efficiency (%)[b]	63	59	54	59	20	20	22	20	20	18	23	20

[a] Consists of the initial amount (137 me) + the amount introduced in the leaching solution (20 me/l).
[b] Exchangeable ion/introduced ion.

Table 3. Ionic balance in the adsorbed phase

Exchangeable ion	Na				Ca				Mg			
Initial amount me/column	137				225				210			
Treatment[a]	1	2	3	4	1	2	3	4	1	2	3	4
Amount of ion at the end of the experiment me/column	31	40	51	47	400	389	378	377	143	144	140	147
Replaced ion me/column	−106	−97	−86	−90	+175	+164	+153	+152	−67	−66	−70	−63
% of exchange	77	70	63	66								

[a] Symbols 1, 2, 3 and 4 are for the 6.8, 1.36, 0.68 and 0.34 N concentrations.

column became from 8.8 meq/100 to less than 1.0 meq/100 gr of soil (ESP of less than 2.5). The differences in the amount of Na replaced in the various treatments is expressed in the depth to which the soil was reclaimed. This clear dividing line is the result of the high soil affinity for calcium ions. In the movement process, any Na ion behind the dividing line is displaced preferentially by Ca ions and will soon catch up with the boundary. Similarly, any Ca ion ahead of the dividing line is preferentially retained by

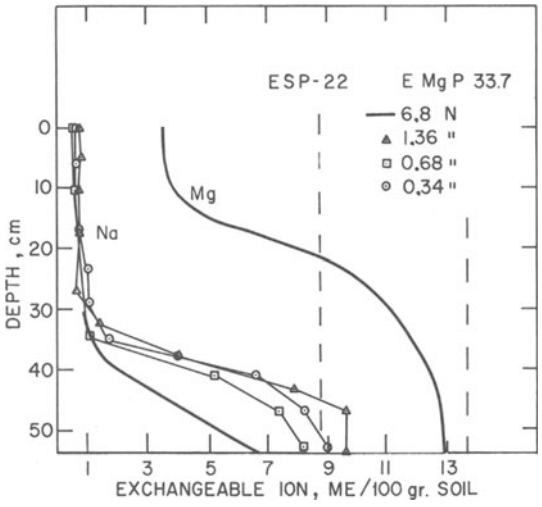

Fig. 5. Na and Mg concentration in the soil profile

soil particles until the line reaches it again. The boundary achieves steadiness when the sharpening effect of equilibrium and the levelling effect of perturbations balance one another.

On the other hand, if equilibrium is unfavorable, as is the case for Ca/Mg exchange, the situation is different. If there is no preference for either of the ions, the Mg ions are not preferentially displaced and remain behind, and any Ca ions ahead of the boundary are not retained by soil particles. Unfavorable equilibrium conditions promote spreading of the boundary line. This effect is clear from the exchangeable Mg concentration profile in the column for high concentration treatment (Fig. 5). The Mg profiles for the other treatment are very similar to the one given and were therefore omitted. Because soil affinity for Mg ions is stronger than that for Na ions, only 30% of adsorbed Mg ions were replaced by Ca ions, and the boundary between reclaimed and unreclaimed soil was spread over a wide depth.

The Effect of Electrolyte Concentration on Na/Ca Exchange Equilibrium

The results in Tables 2 and 3 yielded the conclusion that the most concentrated treatments were also the most efficient in replacing adsorbed Na. This conclusion is in contrast to what might be expected using GAPON'S equation.

The mass action law for the reaction described by Eq. (1) is:

$$K = \frac{(\overline{Na})\,(Ca)^{1/2}}{(\overline{Ca})^{1/2}\,(Na)} \tag{2}$$

where $(\overline{Na})$ and $(\overline{Ca})$ are the equivalent fractions of Na and Ca in the exchange complex, respectively, and (Na) and (Ca) are the concentrations of these ions in the solution. Rearranging Eq. (2) gives:

$$\frac{\overline{Na}}{(\overline{Ca})^{1/2}} = K\frac{(Na)}{(Ca)^{1/2}} \tag{3}$$

In the range of low equivalent fractions of Na in the exchange phase, $(\overline{Ca})$ is close to 1 and $(\overline{Ca})^{1/2}$ can be replaced by $(\overline{Ca})$, thus Eq. (3) becomes:

$$\frac{(\overline{Na})}{(Ca)} = ESR = K\,\frac{Na}{(Ca)^{1/2}} \tag{4}$$

If the concentration of the ions in solution is expressed in mmoles/l, then the quotient on the right is the SAR (Sodium Adsorption Ratio) defined by the U.S. Salinity Laboratory staff (RICHARDS, 1954) and Eq. (4) becomes:

$$ESR = K_G\,(SAR) \tag{5}$$

where K_G is GAPON'S constant.

Analyzing a large number of soil samples, the staff of the Salinity Laboratory gave a value of 0.01475 for GAPON'S constant.

It can be shown that GAPON'S equation predicts that soil affinity for Ca increases with dilution of the solution. A numerical example will demonstrate this point. The SAR of a solution whose Na and Ca concentrations are 1000 meq/l each, is $\frac{1000}{\left(\frac{1000}{2}\right)^{1/2}} = 44.7$ and the corresponding ESR is 0.66.

If this solution is diluted 100 times, the new SAR is $\frac{10}{\frac{10}{2}} = 4.47$ and the corresponding ESR is 0.066.

Thus it might be expected that for a constant amount of $CaCl_2$, the more diluted the solution, the more efficient the replacement of adsorbed Na.

However, our experimental results indicated the opposite trend, and therefore the validity of GAPON'S equation was tested.

A sample of soil was equilibrated with solutions of the same SAR but with total electrolyte concentrations of 50, 100, 1000, and 5000 meq/l. After centrifugation of the soil suspension, the quantity of water per sample was determined, and the cations in the adsorbed and solution phase were replaced by leaching the samples with ammonium 1.0 N solutions (United States Salinity Laboratory Staff, 1954).

The amount of Na and Ca ions in the soil solution phase was calculated from the weight of the solutions and the concentration of ions in the solution (ignoring ion exclusion at this high salt concentration range). The concentrations of ions in the adsorbed phase were calculated and are presented in Table 4 which shows that GAPON'S equation

Table 4. Effect of concentation on Gapon's constant

SAR	Concentration in solution (me/l)			Exchangeable Na me/100 gm	ESP	GAPON'S constant $\times 10^3$
	Na	Ca	Total			
10	32.6	19.1	51.0	4.91	12.2	13.2
	51.6	50.3	102.0	4.88	12.2	13.6
	211.0	812.0	1,023.0	3.36	8.4	8.75
	532.0	4.524.0	5,056.0	2.84	7.1	6.8
20	43.5	9.28	52.8	8.70	21.1	13.2
	78.3	26.80	105.1	8.24	20.5	12.1
	380.0	644.0	1,024.0	4.92	12.3	6.6
	978.0	4,095.0	5,073.0	4.28	10.7	5.6

is not valid at high electrolyte concentrations. It is evident that, with increasing concentrations of the equilibrium solution (for the same SAR), soil affinity for Ca increases. This increase, at very high electrolyte concentrations, is responsible for the high efficiency of high concentration treatments in replacing adsorbed Na from the soil.

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